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<b>(21) International Application Number:</b> PCT/US98/09058 <b>(22) International Filing Date:</b> 1 May 1998 (01.05.98) <b>(30) Priority Data:</b> 60/046,799      2 May 1997 (02.05.97)      US <b>(71) Applicant (for all designated States except US):</b> ADVANCED CHEMICAL DESIGN [US/US]; 489 S. Belvoir Boulevard, Euclid, OH 44121 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> HENRY, Richard, G. [US/US]; 26945 Amhearst Circle, Beachwood, OH 44122 (US). <b>(74) Agent:</b> NAUMAN, Timothy, E.; Fay, Sharpe, Beall, Fagan, Minnich & McKee, 7th floor, 1100 Superior Avenue, Cleveland, OH 44114-2518 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ENVIRONMENTALLY-SAFE SOLVENT COMPOSITIONS UTILIZING 1-BROMOPROPANE THAT ARE STABILIZED, NON-FLAMMABLE, AND HAVE DESIRED SOLVENCY CHARACTERISTICS		
<b>(57) Abstract</b>  Environmentally-safe, low volatile-organic-compound (VOC), solvent compositions containing 1-bromopropane are disclosed. The compositions contain additional compounds to adjust the solvency characteristics and/or stabilize the 1-bromopropane. To adjust the solvency characteristics while inhibiting flammability, n-propanol or hydrofluorocarbon in a precise amount is added. To stabilize the compositions, a variety of stabilizing agents are added, one of which contains: tert-butyl alcohol or n-propanol; dimethoxymethane or diethoxymethane; and a mixture of 2 or more epoxides selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin. The composition is easily used with conventional cleaning techniques and easily incorporated into existing cleaning apparatuses such as vapor degreasers, motion picture film cleaning machines, aerosol applications and the like.		

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ENVIRONMENTALLY-SAFE SOLVENT COMPOSITIONS UTILIZING  
1-BROMOPROPANE THAT ARE STABILIZED, NON-FLAMMABLE, AND HAVE  
DESIRED SOLVENCY CHARACTERISTICS

Cross-Noting to Related Applications

This application is a continuation-in-part of U.S. Patent Application 08/598,798 filed February 9, 1996; claims the benefit of U.S. Provisional Patent Application No. 5 60/046,799, filed May 2, 1997; is a continuation-in-part of U.S. Patent Application 08/818,971 filed March 14, 1997; is a continuation-in-part of U.S. Patent Application 08/932,724 filed September 18, 1997; and is a continuation-in-part of U.S. Patent Application 09/022,779 filed December 2, 1997.

10 Background of the Invention

This invention pertains to the art of solvent compositions and more particularly to solvent compositions that are stable, non-flammable, and environmentally safe.

15 The invention is particularly applicable to cleaning compositions for removing hydrocarbon-soluble contaminants, such as oil, grease, and rosin, from articles using conventional cleaning techniques and will be described with particular reference thereto. However, it will be appreciated that the invention may be advantageously employed 20 with inks, coatings, and adhesives and in lubricant-carrying, spot-free, water drying as well as other environments and applications.

Heretofore, solvent or cleaning compositions have been widely used in immersion cleaning, ultrasonic cleaning, 25 wipe cleaning, aerosol cleaning and vapor degreasing. These techniques involve exposing contaminated articles to a solvent to dissolve and removes contaminants. The contaminants often consist of oil, grease, flux or other

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hydrocarbon-soluble material. In addition, contaminants can include any unwanted non-soluble particles adhering to the hydrocarbon-soluble contaminants.

#### Ozone Depleting Solvents

5           In recent past, solvents of choice for vapor degreasing and ultrasonic cleaning were 1,1,1-trichloroethane and trichloroethylene. Other solvents for cleaning were chlorofluorocarbon solvents such as CFC-113, and various hydrochlorofluorocarbons such HCFC-141B. However, the  
10           problem with these solvents and others is that they are now listed by the United States Environmental Protection Agency as ozone-depleting chemicals and have been or are being phased out of production. In this regard, they all have ozone depleting potentials of 0.1 or greater which makes them  
15           dangerous to the earth's ozone layer and subject to regulation.

#### Volatile Organic Compounds

          Another problem with many hydrocarbon-based solvents is that they form ground-based ozone which can turn  
20           into smog. More particularly, upon evaporation, certain highly-reactive hydrocarbon-based solvents combine with hydroxyl radicals in the presence of ultraviolet (UV) light. When this occurs very close to the ground, it can produce photochemical smog. Smog is harmful and sometimes dangerous  
25           in part because it reduces visibility for drivers of vehicles. Some cities with severe smog actually issue "alerts" to warn drivers. Although smog is partially caused by hydrocarbon emissions from cars, another major contributor is industrial use of hydrocarbon-based solvents such as  
30           hexane and toluene.

          The difference between solvents that form ground-based ozone and those that do not is defined by the reaction

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rate of ethane. If a compound has a reaction rate with the hydroxyl radical and UV light that is faster than ethane, the compound is deemed to react too close to the ground such that it forms ozone and smog. These "highly-reactive" compounds are termed volatile organic compounds (VOCs). On the other hand, if a compound has a reaction rate that is slower than ethane, the compound reaches higher into the atmosphere before reacting with the hydroxyl radical and UV light. In such instances the non-VOC compound does not contribute to the formation of ground based ozone and smog.

#### Flammable Solvents

Other solvents that have been used for cleaning are alcohols. These types of solvents can have sufficient solvency power to completely dissolve unwanted oil, grease or hydrocarbon-soluble contaminants. However, alcohols have limited use because they are flammable.

#### Unstable Solvents

Still another problem with certain solvents is their lack of stability. In this regard, many halogenated solvents decompose in the presence of water and certain metals. The decomposition creates corrosive acids which can attack cleaning apparatuses and articles that the solvents were intended to clean. Further, the decomposition can release harmful gases into the air. The stability is even more of a concern with flammable solvents.

#### Weak Solvents

Still other solvents are less effective because they have low solvency power. Hydrofluorocarbons (HFCs) such as 2,3-dihydroperfluoropentane are non-flammable and exhibit good environmental and toxicological characteristics. This particular HFC solvent has been granted approval under the

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Significant New Alternatives Program (SNAP) by the U.S. Environmental Protection Agency. However, this solvent and HFCs generally have low solvency compared to the chlorinated or brominated solvents. This drawback significantly limits the use of HFCs. One solution has been to mix the HFC with trans-dichloroethylene; however, trans-dichloroethylene can only be added in very low amounts to avoid flammability.

Alcohols such as methanol and isopropanol have also suffer from low solvency power. Hydrochlorofluorocarbon (HCFC) have been added to alcohols in the range of 3.5-7 percent by volume to improve solvency for inorganic flux residue. However, HCFC solvents have been banned under the Montreal Protocol for their inherent ozone depletion potential.

#### Overly Aggressive Solvents

Each solvent has an associated Kauri butanol which is a measure of its solvency power. The higher the Kauri butanol value (kb) the stronger the solvent. Preferably, the Kauri butanol value is high enough to completely dissolve the unwanted oil, grease or hydrocarbon-soluble contaminant. The brominated solvents such as 1-bromopropane and chlorobromomethane have very high Kauri butanol values of around 126-132 which make them particularly effective cleaning agents for metallic materials.

A problem arises if it is desired to clean articles such as printed circuit boards and medical devices which contain plastic or solvent-sensitive material. Cleaning agents such as 1-bromopropane and chlorobromomethane are far too powerful to clean materials containing plastic. For example, 1-bromopropane by itself damages most plastics because of its high Kauri butanol value of 126.

In the past, this problem was addressed by using "gentler" solvents such as the chlorofluorocarbons CFC-113.

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and HCFC-141b. These chlorofluorocarbons have Kauri butanol values of only 30 and 70, respectively. These solvents remove flux and oils from solvent sensitive substrates without attacking and dissolving the substrates or removing identifying markings used in the printed circuit board industry. However, these chlorofluorocarbons are environmentally unsafe in that their ozone depleting potentials are greater than 0.1.

U.S. Patent No. 5,403,507 to Henry discloses cleaning compositions of dibromomethane and stabilizing agents. The compositions have a boiling point of 210 degrees. Although the compositions are effective cleaning agents, their solvency is too high for solvent-sensitive materials. Further, the compositions are no longer considered environmentally safe. They all have ozone depleting potentials of 0.1 or greater which makes them dangerous to the earth's ozone layer and subject to regulation. Still further, the boiling point is too high to clean some heat-sensitive articles.

#### Other Art

Other art attempts to address these concerns without arriving at a practical solution. For example, U.S. Patent No. 4,193,838 to Kelly et al. describes a method in which a pool of hot saturated vapors of a halogenated solvent are used to remove thermoplastic resin. In practice, the method would be very dangerous because the halogenated solvents, which are unstabilized, would become very acidic within minutes. The acidic solvent would then damage the cleaning apparatus and probably any article being cleaned.

U.S. Patent No. 4,115,461 to Archer et al. describes a method for stabilizing non-flammable trichloroethane using a mixture of three stabilizing agents. The agents include 1,4-dioxane, 1,2-butylene oxide, tert-amyl

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alcohol, nitromethane and 1,3-dioxolane. Although these agents may be effective stabilizers with trichloroethane, they are not necessarily effective with other solvents. More importantly, if the solvent is self-extinguishing rather than  
5 non-flammable, the range of stabilizers taught in Archer et al. would make the solvent mixture flammable. This would bar the solvent mixture from being used in many cleaning applications, especially in vapor degreasing.

U.S. Patent No. 5,403,507 to Henry discloses  
10 cleaning compositions of dibromomethane and stabilizing agents. The compositions have a boiling point of 210 degrees. Although the compositions are effective cleaning agents, their solvency is too high for solvent-sensitive materials. Further, the compositions are no longer  
15 considered environmentally safe. They all have ozone depleting potentials of 0.1 or greater which makes them dangerous to the earth's ozone layer and subject to regulation. Still further, the boiling point is too high to clean some heat-sensitive articles.

U.S. Patent No. 4,056,403 issued to Cramer et al.  
20 describes a method and composition for cleaning polyurethane foam generating equipment. The composition includes methylene chloride or other halogenated hydrocarbon and a monohydric alcohol. These compositions have solvencies too  
25 high for solvent-sensitive materials. Further, the compositions have ozone depleting potentials of 0.1 or greater making them subject to regulation.

U.S. Patent No. 3,924,455 to Bergishagen discloses  
30 a method and composition for stripping brittle lacquer coatings from plastic models without damaging the plastic. The composition comprises halogenated solvents, glycol ethers and mineral spirits. This method and composition has several drawbacks. The composition is not stabilized and therefore must be handled carefully to prevent water- and/or metal-



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initiated decomposition. Further, the composition is not environmentally safe. Regarding the method, before applying the stripping composition, the coated plastic must be cleaned with alcohol and allowed to dry for about ½ hour. These additional steps diminish the value of the method.

#### Objects of the Invention

A desired solvent or cleaning composition has the following characteristics: 1) stabilized from decomposition in the presence of water and/or metals; 2) non-flammable at room temperature and/or at temperatures of vapor degreasing; 3) an ozone depletion potential of less than 0.1; 4) a Kauri-Butanol value below 92 so that it will not damage plastics or other solvent-sensitive materials; 5) an evaporation rate of at least 3; and 6) leave no residue on evaporation.

Thus, an object of the present invention is to provide effective cleaning compositions which are suitable for removing hydrocarbon-soluble contaminants from electronic, plastic and metallic materials.

Another object of the present invention is to reduce the Kauri Butanol Value of stabilized and unstabilized cleaning solvents.

Another object of the present invention is to provide solvent compositions which are non-flammable and non-ozone depleting.

Another object of the present invention is to provide a safe "drop in" substitute for cleaning apparatuses and techniques which currently use environmentally unsafe or overly strong solvents.

#### Summary of the Invention

The present invention contemplates a new and

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improved compositions and methods which overcome all of the above referenced problems and others.

5 In accordance with the present invention, there is provided an environmentally-safe, low volatile organic compound (VOC), non-flammable or self-extinguishing, solvent composition. The composition contains: 10-99.99999 %, by total volume of the composition, 1-bromopropane; and one of a stabilizing agent and solvency-adjusting agent.

10 In accordance with a more limited aspect of the invention, the composition contains approximately 4.0-6.4 %, by total volume of the composition, n-propanol, to sufficiently increase a Hansen solubility parameter.

15 In accordance with another more limited aspect of the invention, the solvency-adjusting agent contains approximately 30-90 %, by total volume of the composition, hydrofluorocarbon.

20 In accordance with yet another more limited aspect of the invention, the stabilizing agent is selected from the group consisting of: pyridine; triethylamine; morpholine; n-alkylmorpholines in which the alkyl group has 1-7 carbon atoms; diisoalkylamine having 3-4 carbon atoms; dicyclohexylamine; aliphatic alcohols having 1-10 carbon atoms; propargyl alcohol; glycerol; 3-methyl-pentyn-3-ol; ephichlorohydrin; epibromohydrin; butylene oxide; furan; 25 phenol and its derivatives; ethers having 1-5 carbon atoms; nitroalkanes having 1-7 carbon atoms; and cyclohepto-1,3,5-triene.

30 A principal advantage of the invention is a solvent that is non-flammable, low- or non-VOC and has an ozone depletion potential of less than 0.1.

Another advantage of the invention is an effective cleaning composition for cleaning hydrocarbon-soluble contaminants from articles without damaging those that are solvent-sensitive.

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Another advantage of the invention is that it may be used in place of solvents such as CFC-113 and HCFC-141b in current cleaning apparatuses and techniques without any changes thereto.

5 Still other advantages and benefits of the invention will become apparent to those skilled in the art upon a reading and understanding of the following detailed description.

#### Detailed Description of the Preferred Embodiment

10 The cleaning compositions as herein described and as set forth in the claims are expressed in terms of percentages by volume unless clearly indicated to the contrary.

15 In a preferred embodiment of the present invention, an effective solvent or cleaning composition contains mostly 1-bromopropane also known as n-propyl bromide ("NPB"). This solvent has high solvency power, a low-ozone-depletion potential and is non-VOC.

20 However, full industrial acceptance of 1-bromopropane would remained limited because it easily decomposes in contact with water and certain metals, which causes it to generate corrosive amounts of hydrogen bromide. This decomposition can occur even when the solvent is used in a cold liquid phase, although the decomposition reaction is  
25 more likely to occur at high temperatures and especially in the hot vapor phase. Accordingly, 1-bromopropane should be stabilized.

30 Further, 1-bromopropane has certain other disadvantages which require the addition of other components depending on the application. More particularly, 1-bromopropane is flammable and overly aggressive with solvent-sensitive articles such as plastics. Accordingly, various

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preferred embodiments described below address one or more of the disadvantages of 1-bromopropane.

Non-flammable or self-extinguishing embodiments containing 1-bromopropane That Have a Higher Hanson Solubility Index

5                   1-bromopropane has a boiling point of 71° C and a flash point at 22-24° C. Flash point tests have been performed which show that 1-bromopropane is self-extinguishing at temperatures up to its boiling point. Self-extinguishing means that the solvent has flammable limits in  
10                   air. 1-bromopropane is self-extinguishing in an open cup test in which it has a flash point but not a fire point. In closed cup flash point tests, 1-bromopropane still ignites. Because 1-bromopropane is not completely non-flammable, there are some safety concerns with use of this solvent.

15                   In one non-flammable embodiment, a solvent mixture includes 1-bromopropane and n-propanol. N-propanol is flammable. Accordingly, n-propanol is preferably in an exact amount to decrease the mixture's solvency while still keeping the mixture self-extinguishing. Very small amounts  
20                   of stabilizing agents may also be added if necessary.

                  In Table 1 below, n-propanol is added to 1-bromopropane in very precise amounts. At each amount, the flammability is measured by a TAG Closed Cup method. In addition, the Hansen solubility parameter is shown in the  
25                   table. The Hansen solubility of a solvent is an indication of the solvents relative polarity. The lower the Hansen solubility parameter the more a solvent can dissolve non-polar hydrocarbon materials such as rosin or paraffin oil. The higher the Hansen solubility parameter the better the  
30                   solvent is able to dissolve inorganic materials such as a salt. The Hansen solubility range is usually 6-13 where 6 is the parameter for a compound such as a mineral spirit and 13 is for a compound such as ethanol.

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Table 1.

Test Summary For N-Propanol Plus 1-Bromopropane

	<u>Vol.% n-propanol</u>	<u>Hansen solubility</u>	<u>Flash Point</u>
	3.00	8.2	Self-extinguishes
5	3.10	8.2	Self-extinguishes
	3.20	8.2	Self-extinguishes
	3.30	8.2	Self-extinguishes
	3.40	8.2	Self-extinguishes
	3.50	8.2	Self-extinguishes
10	3.60	8.2	Self-extinguishes
	3.70	8.2	Self-extinguishes
	3.80	8.3	Self-extinguishes
	3.90	8.3	Self-extinguishes
	4.00	8.4	Self-extinguishes
15	4.10	8.4	Self-extinguishes
	4.20	8.4	Self-extinguishes
	4.30	8.4	Self-extinguishes
	4.40	8.4	Self-extinguishes
	4.50	8.4	Self-extinguishes
20	4.60	8.4	Self-extinguishes
	4.70	8.4	Self-extinguishes
	4.80	8.4	Self-extinguishes
	4.90	8.5	Self-extinguishes
	5.00	8.5	Self-extinguishes
25	5.10	8.5	Self-extinguishes
	5.20	8.5	Self-extinguishes
	5.30	8.5	Self-extinguishes
	5.40	8.5	Self-extinguishes

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5.50	8.6	Self-extinguishes
5.60	8.6	Self-extinguishes
5.70	8.6	Self-extinguishes
5.80	8.7	Self-extinguishes
5.90	8.7	Self-extinguishes
6.00	8.8	Self-extinguishes
6.10	8.8	Puffs then after 2 seconds flame goes out
6.30	8.8	Puffs then after 2 seconds flame goes out
6.40	8.8	At 19°C, mixture ignites and continues burning
6.50	8.9	At 19°C, mixture ignites and continues burning
6.60	8.9	At 19°C, mixture ignites and continues burning
6.70	8.9	At 19°C, mixture ignites and continues burning
6.80	8.9	At 19°C, mixture ignites and continues burning
6.90	8.9	At 19°C, mixture ignites and continues burning
7.00	8.9	At 19°C, mixture ignites and continues burning
7.10	8.9	At 19°C, mixture ignites and continues burning

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7.20	8.9	At 19°C, mixture ignites and continues burning
7.30	8.9	At 19°C, mixture ignites and continues burning
7.40	9.00	At 19°C, mixture ignites and continues burning
7.50	9.00	At 19°C, mixture ignites and continues burning

5                   Accordingly, a preferred embodiment includes  
1-bromopropane and 4.0-6.4 vol. % n-propanol. In the above  
chart, this mixture is shown to have a sufficiently increased  
Hansen solubility parameter while remaining self-  
extinguishing. In contrast to other mixtures, this  
10                   embodiment does not create a fire hazard upon extended  
boiling in a vapor degreaser. The preferred combination  
would have the proper amount of n-propanol to give the  
required increase in solubility for inorganic flux residue  
found on circuit boards for example.

15                   In another preferred embodiment, a solvent  
composition comprising 4 percent by volume of n-propanol and  
96 percent of stabilized 1-bromopropane is prepared. After  
a flash point measurement is made it is seen to be self-  
extinguishing. It is then placed in a standard sump type  
20                   vapor degreaser and brought to a boil. A circuit board which  
has been coated with inorganic flux residue is then placed in  
the vapors. After 2 minutes of exposure time the flux  
residue is seen to be removed.

25                   In another preferred embodiment, a solvent  
composition comprising 6.4 percent by volume of n-propanol  
and 93.6 percent of stabilized 1-bromopropane is prepared.  
After a flash point measurement is made it is seen to be

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self-extinguishing. It is then placed in a standard sump type vapor degreaser and brought to a boil. A circuit board which has been coated with inorganic flux residue is then placed in the vapors. After 1 minute of exposure time the flux residue is seen to be removed.

Lower-solvency and Non-flammable Embodiments  
Containing 1-bromopropane

1-bromopropane is very aggressive on plastic substrates where it causes crazing, etching and sometimes dissolves the plastics. This is not acceptable in many sensitive applications such as in electronics where very solvent sensitive plastics are common.

In a preferred embodiment, a hydrofluorocarbon (HFC), which contains only hydrogen, fluorine, and carbon atoms, is mixed with 1-bromopropane in an amount sufficient to make the mixture non-flammable by Tag Closed Cup testing.

In another preferred embodiment, an HFC is mixed with 1-bromopropane in an amount sufficient to make the 1-bromopropane safe for use on plastics substrates.

These and additional embodiments are more particularly shown in the table below. Various mixtures of 1-bromopropane and the HFC were tested for attack on polycarbonate plastic. The plastic was dipped into the solvent mixture for 1 hour and then examined for crazing or etching. The various mixtures were also tested for their flash points by the Tag Closed Cap method.

Table 2.

Test Summary for Hypdrofluorocarbon (HFC)  
Plus 1-Bromopropane (NPB)

<u>NPB + Vol% HFC</u>	<u>crazing or etching</u> <u>on polycarbonate</u>	<u>Flash Point</u>
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5	10	dissolves	22 degrees C.
	15	dissolves	25 degrees C.
	20	dissolves	40 degrees C.
	25	dissolves	46 degrees C.
	30	dissolves	52 degrees C.
10	35	dissolves	58 degrees C.
	40	Crazes	None
	45	Crazes	None
	50	etches	None
	60	Slight etching	None
15	65	Trace	None
	70	No attack	None
	75	No attack	None
	80	No attack	None
	85	No attack	None

Effective cleaning can be done in less than 1 hour, i.e., the test described above represents prolonged immersion in the cleaning composition. When using the cleaning composition, a higher amount of NPB may be added than indicated in the test. Accordingly, desired cleaning embodiments contain the following:

Table 3.

	<u>NPB by vol</u>	<u>Hydrofluorocarbon by vol.</u>
<u>operative range</u>	10-40%	30-90%
<u>preferred range</u>	20-55%	40-85%

In another preferred embodiment, a mixture contains 40% by volume of hydrofluorocarbon solvent and 60% by volume

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of 1-bromopropane. A Tag Closed Cup flash point test was performed and the mixture was found to have no flash point. Thus, the embodiment would be classified as non-flammable.

5 In still another preferred embodiment, a mixture contains 70% by volume of a hydrofluorocarbon solvent and 30% by volume of 1-bromopropane. A piece of polycarbonate plastic was immersed in this mixture for 1 hour and was examined for crazing, etching or dissolving of the plastic. No solvent attack was observed.

10 In yet another preferred embodiment, a mixture contains 40% by volume hydrofluorocarbon solvent, 4% 1,3-dioxolane, 0.5% 1,2 butylene oxide, 0.5% nitromethane and 55% 1-bromopropane is prepared. A Tag Closed Cup flash point test was performed and the mixture was found to have no flash  
15 point. Thus, the embodiment would be classified as non-flammable.

These lower-solvency and non-flammable solvents are useful in aerosol, immersion, or wipe cleaning, lubricant carrying, spot-free water drying and other applications.

20 Stabilized Embodiments Containing 1-Bromopropane

In a preferred stabilized solvent composition, 1-bromopropane is mixed with a stabilizing mixture comprising nitromethane, 1,2-butylene oxide and 1,3-dioxolane. The stabilizing mixture prevents or inhibits the 1-bromopropane  
25 from turning acidic and releasing bromine into the air. Each of the components of the stabilizing solvent mixture is selected to have a low boiling point, preferably around the boiling point of 1-bromopropane.

In another preferred embodiment, the cleaning  
30 composition contains about 95% 1-bromopropane, 4% 1,3-dioxolane, 0.5% 1,2 butylene oxide and 0.5% nitromethane. It is not necessary to have these exact values to obtain the advantages of the present invention.

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0.2% p-tert-amyl phenol  
0.3% 3-methyl-1-pentyn-3-ol

## Example 2

## Stabilizer system:

5        0.1% 5,6,7,8-tetramethyl-5,6,7,8-tetrahydro-2-naphthol  
      0.3% 3-methyl-1-pentyn-3-ol.

Examples 1-2 utilized a combination of a tertiary acetylenic monohydric alcohol and a phenolic compound.

## Example 3

10       Stabilizer system

      0.09% furfuryl alcohol

## Example 4

## Stabilizer system:

      0.012% furfuryl mercaptan

15       Examples 3-4 utilized a small amount of either a cyclic carbinol or a corresponding mercaptan. Concentrations of 0.05-0.5 % by volume provide significant inhibition.

## Example 5

## Stabilizer system:

20       2.0% 1,4-dioxane  
      0.03% styrene oxide

## Example 6

## Stabilizer system:

25       2.0% 1,4-dioxane  
      0.03% phenyl glycidyl ether

## Example 7

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## Stabilizer system:

3.0% 1,3-dioxolane

0.5% nitromethane

0.5% phenyl glycidyl ether

5 Examples 6-7 utilize a primary stabilizer such as styrene oxide, phenyl glycidyl ether and mixture thereof and a second stabilizer from the group of a primary, secondary or tertiary alkanol, a 1-3 carbon atom aliphatic nitro compound, 1,4-dioxane or 1,3-dioxolane.

10 Below are additional preferred embodiments described in percent by volume. One preferred embodiment includes approximately: 1-bromopropane 90-98%; 0.5-6.4% tert-butyl alcohol or n-propanol; 0.1-4% dimethoxymethane or diethoxymethane; 0.1-3% of a mixture of 2 or more epoxides  
15 selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin.

Another preferred embodiment includes approximately: 1-bromopropane 90-98%; 0.5-6% 1,3-dioxolane; 0.1-4% nitromethane or nitroethane; 0.1-3% of a mixture of 2  
20 or more epoxides selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin.

Yet another preferred embodiment includes approximately: 90-98% 1-bromopropane; 0.5-6% 1,3-dioxolane; 0.1-4% nitromethane or nitroethane; 0.001-2% n-ethyl  
25 morpholine or n-methyl pyrrolidone; and 0.1-3% of a mixture of 1 or more epoxides selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin.

30 Still another preferred embodiment includes approximately: 90-98% 1-bromopropane; 0.5-6.4% tert-butyl alcohol or n-propanol; 0.1-4% dimethoxymethane or diethoxymethane; 0.1-3% of a mixture of 2 or more epoxides

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Additional embodiments are described in Table 5 below. Column 1 provides a list of stabilizing agents which can be used in combination with 1-bromopropane to provide an improved cleaning composition. Only a quantity of stabilizer sufficient to retard or to stop the reaction of metals and water with 1-bromopropane needs to be used. The stabilizing agent can be used alone or in combination with the additional component or components listed directly across from it in the third column of Table 5 to form a multi-component stabilizing agent.

The cleaning solution of this invention includes about .00001-10 vol.% of one or more of the stabilizing agents listed in Table 5, with the remainder of the solution being 1-bromopropane. Optimum concentrations of the one or more stabilizing agents range from about 0.1 vol% to about 1.5 vol%. When a stabilizing agent is used in combination with one of the additional components, the total concentration of the stabilizing agent and additional components ranges from about .00001 vol.% to about 10 vol.% and preferably from about 0.1 vol.% to about 1.5 vol%.

Table 5.

Stabilizing Agents  
Used for the Stabilization of 1-bromopropane

<u>Stabilizing Agent</u>	<u>vol.%</u>	<u>Additional Components</u>	<u>vol.%</u>
pyridine	0.001-0.3	butylpyrocatechol	0.001-0.3
triethylamine	0.01-0.3	butylene oxide	0.001-0.3
morpholine	0.1-1.0	phenol	0.001-1.0
n-alkylmorpho- lines in which the alkyl group has 1-7 carbon atoms	0.001-0.1	alkyl phenols in which the alkyl group has 1-7 carbon atoms	0.001-1.0

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5	n-alkylmorpho- lines in which the alkyl group has 1-7 carbon atoms	0.001- 0.1	alkyl phenols in which the alkyl group has 1-7 carbon atoms	0.001- 1.0
10	n-alkylpyrroles in which the alkyl group has 1-7 carbon atoms	0.001- 1.0	tetrahydrofuran, or mono- or bicyclic epoxy compounds	0.01-1.0
15	diisoalkylamine s having 3-4 carbon atoms	0.001- 1.0	alkylphenol, in which the alkyl group has 1-7 carbon atoms, or aliphatic alcohols having 1-10 carbon atoms, straight chain or branched chain ketones having 1-10 carbon atoms	0.001- 1.0
	dicyclohexyla- mine	0.001- 0.5	mono- or bicyclic epoxy compds. or phenol	0.01.10
	aliphatic alcohols having 1-10 carbon atoms	0.1- 4.0	nitro compds. or phenol and its derivatives including naphthols	0.05-1.0
20	propargyl alcohol	0.001- 1.0	epichlorohydrin, nitromethane, N-methyl pyrrole or 1,1- dialkylhydrazine in which the alkyl group has 1-10 carbon atoms	0.001- 0.5
	glycerol	0.001- 1.0	phenol and its derivatives, mono- or bicyclic epoxy compds., diisopropyl-amine	0.001- 1.0
	3-methyl- pentyn-3-ol	0.3- 1.0	epichlorohydrin, dihydroxybutane, or phenol	0.05-1.0
25	epichlorohydrin	0.002- 0.5	aliphatic amines having 1-5 carbon atoms, propargyl alcohol, or nitroalkanes having 1-7 carbon atoms, or phenol	0.001- 0.5

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	epibromohydrin	0.002- 0.5	n-methylmorpholine or allyl glycidyl ether in which the allyl group has 1-10 carbon atoms	0.001- 0.5
	butylene oxide	0.25- 0.5	phenols and its derivatives, lactams, oximes, hydrazones, disulfides, acetals, amines	0.001- 1.0
	furan	1.0- 10.0	phenyl glycidyl ether, aliphatic nitro compds. having 1-7 carbon atoms or acetals	0.005- 0.5
5	phenol and derivatives	0.02- 1.0	amines having 1-7 carbon atoms, aliphatic alcohols having 1-10 carbon atoms, or epichlorohydrin	0.0001- 10.0
	ethers having 1-5 carbon atoms	0.05- 5.0	diethylethanolamine	0.1-5.0
10	nitroalkanes having 1-7 carbon atoms	0.01- 5.0	pyrrole and its derivatives or phenol	0.1-5.0
	cyclohepta- 1,3,5-triene	0.01- 5.0	unsaturated tertiary amines having 1-10 carbon atoms	0.03-0.6
	1,4-dioxane	1.0- 10.0	styrene oxide or phenyl glycidyl ether	0.001- 5.0

15 Additional preferred embodiments are listed below  
as examples. These examples inhibit the decomposition of 1-  
bromopropane. All examples include 1-bromopropane as the  
balance of the mixture.

Example 1

20 Stabilizer system:

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selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin.

5 Another preferred embodiment includes 1-bromopropane and approximately 0.00001 vol% to about 10 vol% of at least one multi-component stabilizing agent consisting essentially of:

(a) tert butyl alcohol;

(b) one or more of dimethoxymethane and diethoxymethane; and,

(c) one or more of:

(i) one or more of butylene oxide, propylene oxide and cyclohexene oxide; and,

(ii) one or more of epibromohydrin and epichlorohydrin.

Another preferred embodiment includes 1-bromopropane and approximately 0.00001 vol% to about 10 vol% of:

(a) tert butyl alcohol;

(b) one or more of dimethoxymethane and diethoxymethane; and,

(c) one or more of:

(i) one or more of butylene oxide, propylene oxide and cyclohexene oxide; and,

(ii) one or more of epibromohydrin and epichlorohydrin.

Another preferred embodiment includes 1-bromopropane and approximately, by total volume of the composition:

(a) 1-10% tert butyl alcohol;

(b) 0.1-10% one or more of dimethoxymethane and diethoxymethane; and,

(c) one or more of:

(i) 0.1-5% one or more of butylene oxide, propylene oxide and cyclohexene oxide; and,



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(ii) 0.001-2% one or more of epibromohydrin and epichlorohydrin.

Another preferred embodiment includes 1-bromopropane and approximately, by total volume of the composition:

(a) 1% tert-butyl alcohol or isopropyl alcohol or propyl alcohol;

(b) 0.1% one or more of dimethoxymethane and diethoxymethane; and,

(c) 0.5% or more of a mixture of butylene oxide and cyclohexene oxide.

Another preferred embodiment includes 1-bromopropane and approximately 0.00001 vol% to about 5 vol% one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

Another preferred embodiment includes 1-bromopropane and approximately 0.1-5 vol% one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

Another preferred embodiment includes 1-bromopropane and approximately 0.001-2%, by total volume of the composition, one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

Another preferred embodiment includes 1-bromopropane and approximately 0.01 %, by total volume of the composition, one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

Another preferred embodiment includes 1-bromopropane and approximately, by total volume of the composition:

0.01 % epibromohydrin or epichlorohydrin; and

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0.2 % n-ethyl morpholine.

Another preferred embodiment includes 1-bromopropane and approximately, by total volume of the composition:

0.01 % epibromo or epichlorohydrin;

0.2 % n-ethyl morpholine; and

0.1-1 % propargyl alcohol.

In another preferred embodiment, a stabilized solvent mixture contains 1-bromopropane and a stabilizer mixture of, by total volume, approximately 0.5-3% alcohol such as isopropyl alcohol, 0.01-0.1% cyclohexene oxide, 0.1-1% butylene oxide, 1-5% 1,3-dioxolane, and 0.1-1% dimethoxymethane.

Other preferred embodiments of the 1-bromopropane mixtures include one or more of n-propanol and hydrofluorocarbon to adjust the solvency of the mixture. In addition, the stabilizing agents described above are added to the mixtures to prevent decomposition of the 1-bromopropane.

The 1-bromopropane mixtures can be used to clean metals, plastics, elastomers and circuit boards using various known cleaning apparatuses and techniques. One example technique is vapor degreasing which is described in U.S. Patent No. 5,403,507 to Henry. Another example technique combines vapor cleaning with agitation of the articles as described in U.S. Patent No. 4,193,838 to Kelly et al. Another example is immersion cleaning in which articles are immersed in a bath of the cleaning composition. The bath or articles or both may be agitated to hasten the cleaning process. Another example is ultrasonic cleaning. Other examples are wipe cleaning and aerosol cleaning.

More particularly, in a preferred method of the present invention, the preferred cleaning composition described above is used to clean contaminated printed circuit boards. Other compositions described herein as well as those

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encompassed by the present invention may be used with this preferred method. The boards are contaminated with solder flux composed of epoxy resin. The flux as well as unwanted materials embedded in the flux must be removed. The boards themselves as well as the electronic components on the boards contain plastic or solvent-sensitive materials which must be preserved. Further, the boards and components have various identifying ink markings on them which must be maintained.

The preferred cleaning composition is introduced into a sump of a standard vapor degreaser of the kind described in U.S. Patent No. 5,403,507 to Henry. The composition is brought to a boil by heating to 156 degrees Fahrenheit. The contaminated boards are immersed in the vapor layer of the degreaser for approximately 5 minutes. The boards are then removed from the vapor layer. The solvent of the cleaning composition does not crack, pit, leach or otherwise attack the boards or the components. Further, the solvent does not remove or fade the ink markings. Nevertheless, the board and components are cleaned of all the solder flux.

However, when a mixture of only 95% 1-bromopropane, 0.5% butylene oxide, 0.5% nitromethane and 4% 1,3-dioxolane is used in the degreaser, the high solvency mixture damages the printed circuit boards. Specifically, although the mixture removes the flux, the mixture causes cracking and peeling of the plastic on the board. Moreover, all of the identifying ink markings are removed. The circuit boards are no longer useful for their original purpose.

In another preferred method, a stabilized solvent composition of 90% 1-bromopropane, 0.5% 1,2 butylene oxide, 0.5% nitromethane, 4% 1,3-dioxolane and 5% glycol ether is used to clean motion picture film. The film is contaminated with fingerprints and other oil. The composition is introduced into the sump of a film cleaning machine. The

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sump heats the solvent to a boil. Motion picture film made of cellulose acetate is immersed in the vapor layer of the boiling sump for approximately 60 seconds. In this time, a conventional solvent would attack the film by, for example, bending and/or blurring the film. However, the cleaning composition does not damage the film. Moreover, the cleaning composition removes fingerprints and other oil on the film.

Analogously, the same composition is also suitable for cleaning plastic articles or substrates in ultrasonic cleaning units. In this technique, contaminated articles are immersed in a bath of the cleaning composition. Ultrasound, i.e., high-frequency sound, is transmitted into the bath to clean the articles by causing cavitation in the cleaning composition at the surface of the contaminated articles.

In another preferred method of the present invention, a cleaning composition encompassed in the above disclosure is charged into an aerosol can or other aerosol delivery system. If the can or system is susceptible to attack, it is preferable to use one of the stabilized cleaning compositions. The composition is sprayed onto a contaminated article such as a printed circuit board contaminated with rosin. The spray dissolves and completely removes the rosin. This technique does not damage printed circuit boards, or components or markings thereon.

The invention has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon a reading and understanding of this specification. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

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Having thus described the invention, it is claimed:

1. An environmentally-safe, low volatile organic compound (VOC), non-flammable or self-extinguishing, solvent composition having an ozone depletion potential of less than 0.1, the composition comprising:  
5           10-99.99999 %, by total volume of the composition, 1-bromopropane; and,  
          one of a stabilizing agent and solvency-adjusting agent.
2. A composition according to claim 1 wherein the solvency-adjusting agent comprises approximately 4.0-6.4 %, by total volume of the composition, n-propanol, to sufficiently increase a Hansen solubility parameter.
3. A composition according to claim 2 wherein the solvency-adjusting agent comprises approximately 30-90 %, by total volume of the composition, hydrofluorocarbon.
4. A composition according to claim 2 wherein the solvency-adjusting agent comprises approximately 40-85 %, by total volume of the composition, hydrofluorocarbon.
5. A composition according to claim 1 wherein the stabilizing agent comprises one or more of:  
          1,2-butylene oxide;  
          nitromethane; and  
5           1,3-dioxolane.
6. A composition according to claim 3 wherein the stabilizing agent comprises approximately 0.5-5%, by total volume of the composition, of one or more of:

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5           1,2 butylene oxide;  
          nitromethane; and  
          1,3-dioxolane.

7. A composition according to claim 6 wherein the composition consists essentially of, by total volume of the composition, approximately:

5           40 % hydrofluorocarbon;  
          50 % 1-bromopropane;  
          4% 1,3-dioxolane;  
          0.5% 1,2 butylene oxide; and  
          0.5% nitromethane.

8. A composition according to claim 1 wherein the stabilizing agent consists essentially of approximately, 0.00001-10 %, by total volume of the composition:

5           (a) tert-butyl alcohol;  
          (b) one or more of dimethoxymethane and diethoxymethane; and,  
          (c) one or more of:  
              (i) one or more of butylene oxide, propylene oxide and cyclohexene oxide; and,  
10           (ii) one or more of epibromohydrin and epichlorohydrin.

9. A composition according to claim 1 wherein the stabilizing agent consists essentially of, approximately, by total volume of the composition:

5           (a) 1-10% tert-butyl alcohol or isopropyl alcohol or propyl alcohol;  
          (b) 0.1-10% one or more of dimethoxymethane and diethoxymethane; and,  
          (c) 0.1-5% one or more of a mixture of butylene oxide and cyclohexene oxide.

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10. A composition according to claim 9 wherein the stabilizing agent consists essentially of, approximately, by total volume of the composition:

- 5 (a) 1% tert-butyl alcohol or isopropyl alcohol or propyl alcohol;  
(b) 0.1% one or more of dimethoxymethane and diethoxymethane; and,  
(c) 0.5% or more of a mixture of butylene oxide and cyclohexene oxide.

11. A composition according to claim 1 wherein the stabilizing agent consists essentially of approximately 0.00001-5 %, by total volume of the composition, one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

12. A composition according to claim 11 wherein the stabilizing agent consists essentially of, approximately 0.1-5, by total volume of the composition, of one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

13. A composition according to claim 11 wherein the stabilizing agent consists essentially of approximately 0.001-2%, by total volume of the composition, of one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

14. A composition according to claim 1 wherein the stabilizing agent consists essentially of:

- 5 approximately .01 %, by total volume of the composition, of one or more of epibromohydrin, epichlorohydrin and n-ethyl morpholine.

15. A composition according to claim 14 wherein the stabilizing agent consists essentially of, by total volume of

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the composition:

- 5           0.01 % epibromohydrin or epichlorhydrin  
          0.2 % n-ethyl morpholine.

16. A composition according to claim 1 wherein the stabilizing agent consists essentially of, by total volume of the composition, approximately:

- 5           0.01 % epibromohydrin or epichlorhydrin;  
          0.2 % n-ethyl morpholine; and  
          0.1-1 % propargyl alcohol.

17. A composition according to claim 1 wherein the stabilizing agent is selected from the group consisting of: pyridine; triethylamine; morpholine; n-alkylmorpholines in which the alkyl group has 1-7 carbon atoms; diisoalkylamine  
5           having 3-4 carbon atoms; dicyclohexylamine; aliphatic  
          alcohols having 1-10 carbon atoms; propargyl alcohol;  
          glycerol; 3-methyl-pentyn-3-ol; ephichlorohydrin;  
          epibromohydrin; butylene oxide; furan; phenol and its  
          derivatives; ethers having 1-5 carbon atoms; nitroalkanes  
10          having 1-7 carbon atoms; and cyclohepto-1,3,5-triene.

18. A composition according to claim 1 wherein the composition further comprises at least one additional component present in combination with the stabilizing agent to form a multi-component stabilizing agent wherein the  
5           multi-component stabilizing agent is selected from the group  
          consisting of: pyridine and butylpyrocatechol; triethylamine  
          and butylene oxide; morpholine and phenol; n-alkylmorpholines  
          in which the alkyl group has 1-7 carbon atoms and alkyl  
          phenols in which the alkyl group has 1-7 carbon atoms; n-  
10          alkylpyrroles in which the alkyl group has 1-7 carbon atoms  
          and tetrahydrofuran; n-alkylpyrroles in which the alkyl group  
          has 1-7 carbon atoms and tetrahydrofuran; n-alkylpyrroles in



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15 which the alkyl group has 1-7 carbon atoms and mono- or  
bicyclic epoxy compounds; diisoalkylamines in which the alkyl  
group has 3-4 carbon atoms and alkylphenol in which the alkyl  
group has 1-7 carbon atoms; diisoalkylamines having 3-4  
carbon atoms and aliphatic alcohols having 1-10 carbon atoms;  
20 diisoalkylamines having 3-4 carbon atoms and straight or  
branched chain ketones having 1-10 carbon atoms;  
dicyclohexylamine and mono- or bicyclic epoxy compounds;  
dicyclohexylamine and phenol; aliphatic alcohols having 1-10  
carbon atoms and nitro compounds; aliphatic alcohols having  
25 1-10 carbon atoms and phenol and its derivatives; propargyl  
alcohol and epichlorohydrin; propargyl alcohol and methyl  
pyrrole; propargyl alcohol and 1,1-dialkylhydrazine in which  
the alkyl group has 1-7 carbon atoms; glycerol and phenol  
and its derivatives; glycerol and mono- or bicyclic epoxy  
compounds; glycerol and diisopropylamine; 3-methyl-pentyn-3-  
ol and epichlorohydrin; 3-methyl-pentyn-3-ol and  
30 dihydrooxybutane; 3-methyl-pentyn-3-ol and phenol;  
epichlorohydrin and aliphatic amines having 1-5 carbon atoms;  
epichlorohydrin and nitroalkanes having 1-7 carbon atoms;  
epichlorohydrin and phenol; epibromohydrin and n-  
methylemorpholine; epibromohydrin and allyl-glycidyl ether in  
35 which the allyl group has 1-10 carbon atoms; butylene oxide  
and phenol and its derivatives; butylene oxide and lactams;  
butylene oxide and oximes; butylene oxide and hydrazones;  
butylene oxide and disulfides; butylene oxide and acetals;  
and butylene oxide and amines; furan and phenyl glycidyl  
40 ether; furan and aliphatic nitro compounds having 1-7 carbon  
atoms; furan and acetals; phenol and its derivatives and  
amines having 1-7 carbon atoms; phenol and its derivatives  
and alcohols having 1-10 carbon atoms; phenol and  
epichlorohydrin; ethers having 1-5 carbon atoms and  
45 diethylethanolamine; nitroalkanes having 1-7 carbon atoms and  
pyrrole and its derivatives; nitroalkanes having 1-7 carbon

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50 atoms and phenol; nitroalkanes having 1-7 carbon atoms, 1,3-dioxolane and phenyl glycidyl ether; cyclohepta-1,3,5-triene and unsaturated tertiary amines having 1-10 carbon atoms; and 1,4-dioxane and styrene oxide.

19. A composition according to claim 1 wherein the stabilizing agent consists essentially of, by total volume of the composition, approximately:

- 5 0.5-6.4% tert-butyl alcohol or n-propanol;  
0.1-4% dimethoxymethane or diethoxymethane;  
0.1-3% of a mixture of 2 or more epoxides selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin.

20. A composition according to claim 1 wherein the stabilizing agent consists essentially of, by total volume of the composition, approximately:

- 5 0.5-6% 1,3-dioxolane;  
0.1-4% nitromethane or nitroethane;  
0.1-3% of a mixture of 2 or more epoxides selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, epibromohydrin.

21. A composition according to claim 1 wherein the stabilizing agent consists essentially of, by total volume of the composition, approximately:

- 5 0.5-6% 1,3-dioxolane;  
0.1-4% nitromethane or nitroethane;  
0.001-2% n-ethyl morpholine or n-methyl pyrrolidone;  
0.1-3% of a mixture of 1 or more epoxides selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin.

22. A composition according to claim 1 wherein the

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stabilizing agent consists essentially of, by total volume of the composition, approximately:

- 0.5-6.4% tert-butyl alcohol or n-propanol;
- 5      0.1-4% dimethoxymethane or diethoxymethane; and
- 0.1-3% of a mixture of 2 or more epoxides selected from the group: butylene oxide, propylene oxide, cyclohexene oxide, epichlorohydrin, and epibromohydrin.

23. A composition according to claim 1 wherein the stabilizing agent consists essentially of, by total volume of the composition, approximately:

- 0.5-3% alcohol;
- 5      0.01-0.1% cyclohexene oxide;
- 0.1-1% butylene oxide;
- 1-5% 1,3-dioxolane; and
- 0.1-1% dimethoxymethane.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/09058

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>														
IPC(6) :C11D 7/30, 3/24														
US CL :512/412, 255, 256, 258, 273, 365; 134/40; 252/364														
According to International Patent Classification (IPC) or to both national classification and IPC														
<b>B. FIELDS SEARCHED</b>														
Minimum documentation searched (classification system followed by classification symbols)														
U.S. : 512/412, 255, 256, 258, 273, 365; 134/40; 252/364														
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched														
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)														
Please See Extra Sheet.														
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>														
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X -- Y	WO 96/36688 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 21 November 1996, see examples 29, 70, and 112.	1,3-4,17 ----- 6-7												
X -- Y	WO 96/36689 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 21 November 1996, see examples 44, 90, and 140.	1,3-4,17 ----- 6-7												
X -- Y	US 5,616,549 A (Clark) 01 April 1997, see entire document.	1,5,17-18 ----- 6-7,20,23												
Y	US 5,607,912 A (Samejima et al) 04 March 1997, see entire document.	5-23												
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.														
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*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art													
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*g* document member of the same patent family													
*O* document referring to an oral disclosure, use, exhibition or other means														
*P* document published prior to the international filing date but later than the priority date claimed														
Date of the actual completion of the international search		Date of mailing of the international search report												
22 JULY 1998		14 AUG 1998												
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer ARLEN SODERQUIST Telephone No. (703) 308-0661												

## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US98/09058

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 5,492,645 A (Oshima et al) 20 February 1996 see entire document.	1,5,11-15,17-18 ----- 6-10,16,19-23
Y	US 5,403,507 A (Henry) 04 April 1995, see entire document.	5-23
Y	US 4,056,403 A (Cramer et al) 01 November 1977, see entire document.	1-2
X	JP 7-150197 A (DIPSOL KK) 13 June 1995, see entire document.	1,5,17
X	JP 8-337795 A (TOSOH CORP) 24 December 1996, see entire document.	1,5,17
X,P	US 5,665,170 A (Lee et al) 09 September 1997, see entire document.	1,5,17

# INTERNATIONAL SEARCH REPORT

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PCT/US98/09058

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS and CA and REGISTRY files of STN

search terms: bromopropane, propyl bromide, 1-bromopropane, 1-propyl bromide, stabiliz?, solvenc?, broh2ch2hc3, ch3ch2ch2br, c3h7br, viscosity, azeetro?, epibromohydrin, epichlorohydrin, morpholine, t, butyl alcohol, butanol, isopropyl alcohol, isopropanol, butylene, cyclohexene, oxide, propanol, propyl alcohol